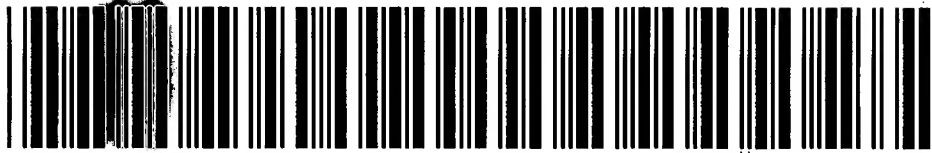# IDS REFERENCES

FOR

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(71) Applicant(s)
Chevron U.S.A. INC
(Incorporated in USA - Delaware)
2613 Camino Ramon, San Ramon,
California 94583-4289, United States of America

(72) Inventor(s)
Charles L Kibby

(74) Agent and/or Address for Service
Haseltine Lake & Co
Imperial House, 15-19 Kingsway, LONDON,
WC2B 6UD, United Kingdom

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US 4624968 A
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(B.ZHONG ET AL)

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(54) Abstract Title
Multi stage Fischer-Tropsch process for the synthetic preparation of liquid fuels

(57) An integrated process for producing liquid fuels from syngas via a two-stage Fischer-Tropsch reaction is disclosed. The first stage of the Fischer-Tropsch chemistry is performed using conditions in which chain growth probabilities are relatively low to moderate, and the product of the reaction includes a relatively high proportion of low molecular (C_{2-8}) weight olefins and a relatively low proportion of high molecular weight ($C_{30}+$) waxes. The product from the first stage is fed into the second stage where the chain growth probabilities are relatively high. The wax and other paraffins produced in the first reaction are largely inert under these conditions. The light olefins compete with heavier olefins for chain initiation, and fewer chains will be initiated at $C_{20}+$. With most chains initiated at C_{2-8}, moderate chain growth probability will produce a relatively larger fraction in the C_{5-12} range. In this manner, wax yield is minimized.
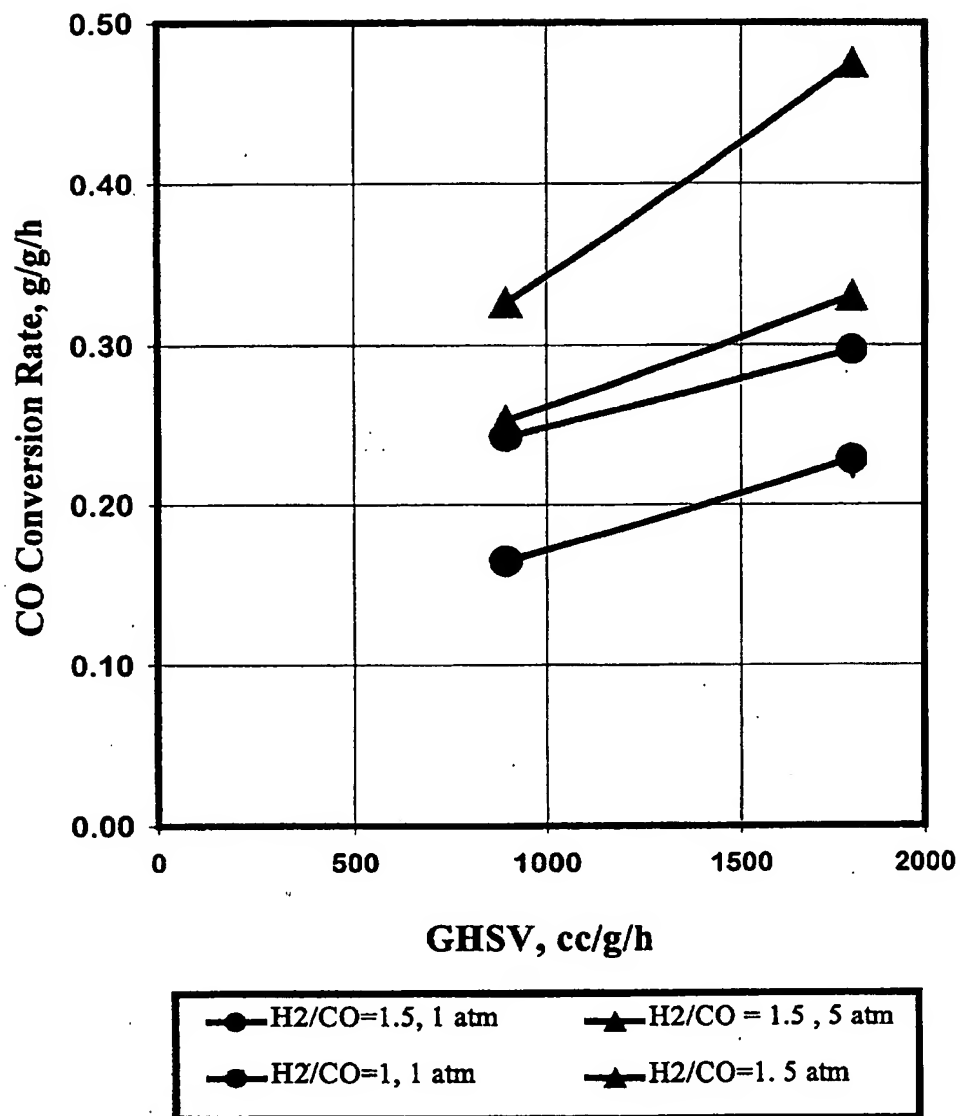
FIGURE 4
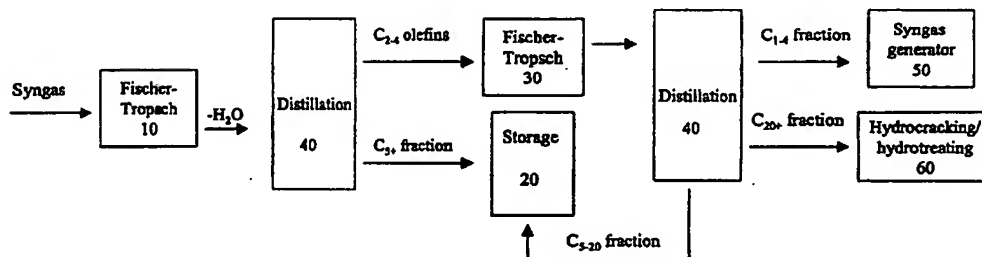
GB 2 359 819 A

Figure 1. CO Conversion vs GHSV

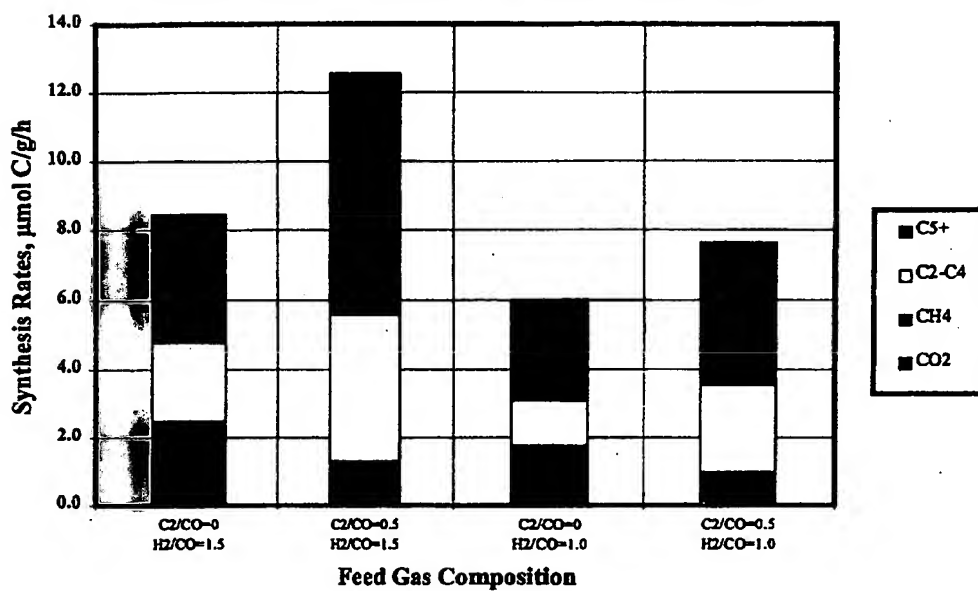## Figure 2. Synthesis Rates 1 atm, 200°C, 1800 cc/g/h

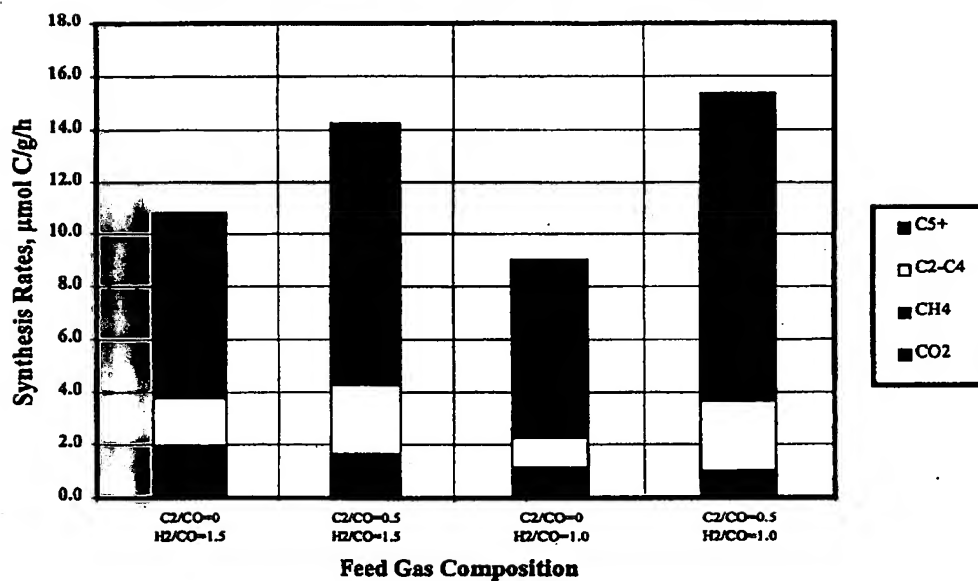Figure 2. Synthesis Rates 1 atm, 200°C, 1800 cc/g/h

Figure 3. Synthesis Rates 5 atm, 200°C, 1800 cc/g/h

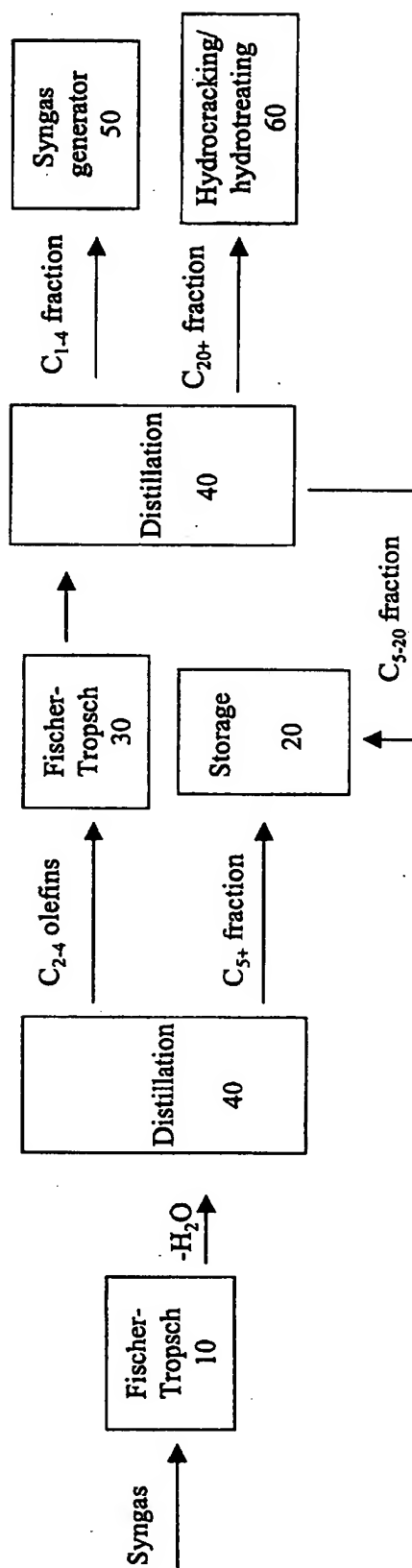Figure 3. Synthesis Rates 5 atm, 200°C, 1800 cc/g/h

FIGURE 4

1   **INCREASED LIQUID SENSITIVITY DURING FISCHER-TROPSCH**

2   **SYNTHESIS BY OLEFIN INCORPORATION**

3

4   <u>BACKGROUND OF THE INVENTION</u>

5

6   The majority of combustible fuel used in the world today is derived from crude

7   oil. There are several limitations to using crude oil as a fuel source. Crude oil

8   is in limited supply; it includes aromatic compounds believed to cause cancer,

9   and contains sulfur and nitrogen-containing compounds that can adversely

10 affect the environment, for example, by producing acid rain.

11

12 Combustible liquid fuels can also be prepared from natural gas. This involves

13 converting the natural gas, which is mostly methane, to synthesis gas, or

14 syngas, which is a mixture of carbon monoxide and hydrogen. An advantage

15 of using fuels prepared from syngas is that they do not contain nitrogen and

16 sulfur and generally do not contain aromatic compounds. Accordingly, they

17 have minimal health and environmental impact.

18

19 Fischer-Tropsch chemistry is typically used to convert the syngas to a product

20 stream that includes combustible fuel, among other products. A limitation

21 associated with Fischer-Tropsch chemistry is that it tends to produce a broad

22 spectrum of products, ranging from methane to wax. Product slates for

23 syngas conversion over Fischer-Tropsch catalysts (Fe, Co and Ru) are

24 controlled by polymerization kinetics with fairly constant chain growth

25 probabilities, which fix the possible product distributions. Heavy products with

26 a relatively high wax content are produced when chain growth probabilities

27 are high. Methane is produced with high selectivity when chain growth

28 probabilities are low.

29

30 Methane can be recirculated to ultimately yield combustible liquid fuel. Wax

31 can be processed, for example, by hydrocracking and/or hydrotreating

32 followed by oligomerization, to yield combustible liquid fuel. However, it would

1   be advantageous to have new methods for providing a product stream from a

2   Fischer-Tropsch process that has a higher proportion of combustible liquid

3   fuel with less methane to recirculate and less wax to process.

4

5   One method used in the past to minimize methane production has been to

6   incorporate olefins in the Fischer-Tropsch reaction. Work in the early 1930's

7   used a roughly 1:1 ratio of hydrogen/carbon monoxide, and added olefins to

8   the reaction mixture (Smith et al., *J.A.C.S.*, 52:3221 (1930). This tended to

9   provide oxygenated material, which is not preferred. U.S. Patent

10 No. 4,754,092 to Iglesia et al. discloses incorporating olefins into a

11 Fischer-Tropsch reaction, but does not specify the type of chain growth

12 probabilities for the reaction, and discloses using a wide range of

13 hydrogen/carbon monoxide ratios such that it would be difficult to predict

14 whether the product would be oxygenated, olefinic, or saturated.

15

16 It would be advantageous to provide methods for improving product yields in

17 Fischer-Tropsch reactions, while minimizing methane and oxygenate

18 production. The present invention provides such methods.

19

20   SUMMARY OF THE INVENTION

21

22 In its broadest aspect, the present invention is directed to an integrated·

23 process for producing liquid fuels from syngas via a two-stage

24 Fischer-Tropsch reaction. The first stage of the Fischer-Tropsch chemistry is

25 performed using conditions in which chain growth probabilities are relatively

26 low to moderate, and the product of the reaction includes a relatively high

27 proportion of low molecular (C_{2-8}) weight olefins and a relatively low proportion

28 of high molecular weight ($C_{30}+$) waxes.

29

30 The products of the first stage include methane, C_{2-4} hydrocarbons, C_5+

31 hydrocarbons, water and carbon dioxide, as well as unreacted syngas.

32 Optionally, but preferably, water produced in the first stage is substantially

1 removed before the product stream is sent to the second stage. Optionally,

2 the product is hydrotreated at this stage to remove any oxygenated products.

3 Further, C_5+ hydrocarbons are preferably isolated. In one embodiment, at

4 least a portion of the olefins is isomerized prior to being fed into the second

5 stage.

6

7 The product from the first stage, after any optionally performed processing

8 steps, is then fed into the second stage where the chain growth probabilities

9 are relatively high. The wax and other paraffins produced in the first reaction

10 are largely inert under these conditions. The light olefins compete with

11 heavier olefins for chain initiation, and fewer chains will be initiated at C_{20}+.

12 With most chains initiated at C_{2-8}, moderate chain growth probability will

13 produce a relatively larger fraction in the C_{5-12} range. In this manner, wax

14 yield is minimized.

15

16 The syngas used in both stages preferably contains certain ratios of hydrogen

17 to carbon monoxide. In the first stage, hydrogen/carbon monoxide ratios in

18 excess of about 1.0/1.0 tend to provide less olefins and more hydrogenated

19 products, although changing the temperature and/or pressure may mitigate

20 these effects to some degree. In the second stage, using a cobalt-containing

21 catalyst, a ratio of hydrogen to carbon monoxide greater than 1.5/1.0 tends to

22 provide a product that is greater than 80% saturated. At a ratio of about

23 1.0/1.0, the product tends to include oxygenates and olefins.

24

25 In one embodiment, the Fischer-Tropsch synthesis with low to moderate chain

26 growth probability is performed using an iron-containing catalyst in the first

27 reactor, and Fischer-Tropsch synthesis with high chain growth probability is

28 performed using a cobalt-containing catalyst in the second reactor.

29

1   <u>BRIEF DESCRIPTION OF THE DRAWINGS</u>

2

3   Figure 1 is a graph comparing the CO conversion (%) vs gas hourly space

4   velocity (GHSV) for the reaction in Example 1.

5   Figure 2 is a graph comparing the synthesis rates (μmol C/g/h) vs feed gas

6   composition for those experiments in Example 1 run at a pressure of 1 atm, a

7   temperature of 200°C, and a GHSV of 1800 cc/g/h. The dark portion of the

8   bar represents the C_5+ fraction. The white portion of the bar represents the

9   C_{2-4} fraction. The gray portion of the bar represents the CH_4 fraction. The

10   gray portion of the bar with diagonal lines through it represents the CO_2

11   fraction.

12

13   Figure 3 is a graph comparing the synthesis rates (μmol C/g/h) vs feed gas

14   composition for those experiments in Example 1 run at a pressure of 5 atm, a

15   temperature of 200°C, and a GHSV of 1800 cc/g/h. The dark portion of the

16   bar represents the C_5+ fraction. The white portion of the bar represents the

17   C_{2-4} fraction. The gray portion of the bar represents the CH_4 fraction. The

18   gray portion of the bar with diagonal lines through it represents the CO_2

19   fraction.

20

21   Figure 4 is a schematic flow diagram representing one embodiment of the

22   invention.

23

24   <u>DETAILED DESCRIPTION OF THE INVENTION</u>

25

26   The present invention is directed to an integrated process for producing liquid

27   fuels from syngas. As used herein, the term "integrated process" refers to a

28   process comprising a sequence of steps, some of which may be parallel to

29   other steps in the process, but which are interrelated or somehow dependent

30   upon either earlier or later steps in the total process.

31

1   In Fischer-Tropsch chemistry, products with a relatively high molecular weight

2   and with a relatively high selectivity for wax are produced when chain growth

3   probabilities are high. Methane and lower molecular weight products,

4   including a variety of low molecular weight (C_{2-8}) olefins, are produced with

5   high selectivity when chain growth probabilities are low.

6

7   The process described herein includes a two stage Fischer-Tropsch reaction.

8   The first stage of the Fischer-Tropsch chemistry is performed using conditions

9   in which chain growth probabilities are relatively low to moderate, and the

10   product of the reaction includes a relatively high proportion of low molecular

11   (C_{2-8}) weight olefins and a relatively low proportion of high molecular weight

12   ($C_{30}+$) waxes. For example, catalysts with low alpha values, i.e., between

13   about 0.600 and 0.700, provide a relatively high proportion of low molecular

14   weight olefins and a relatively low amount of wax, i.e., less than about 10% by

15   weight. Catalysts with moderate alpha values, i.e., between 0.700 and 0.800,

16   provide a moderate proportion of low molecular weight olefins and a moderate

17   amount of wax, i.e., between about 2 and 10% by weight.

18

19   The products of this reaction are fed into the second stage where the chain

20   growth probabilities are relatively high, for example, using catalysts with an

21   alpha value above about 0.800, and preferably, above about 0.850. As a

22   general rule, as the alpha value of the catalyst increases, the amount of

23   methane production decreases.

24

25   Paraffins produced in the first reaction are largely inert under these

26   conditions. The low molecular weight (C_{2-8}, preferably C_{2-4}) olefins compete

27   with heavier molecular weight olefins for chain initiation, and fewer chains are

28   initiated at $C_{20}+$ than if syngas alone is used as feed for a Fischer-Tropsch

29   reaction using the same catalyst.

30

31   Using the process described herein, most chains in the second stage of the

32   Fischer-Tropsch process are initiated at C_{2-8}, resulting in moderate chain

1 growth probability which produces a relatively larger fraction in the C_{5-12}

2 range. In this manner, wax yield is minimized. One of the benefits of

3 performing the two-stage Fischer-Tropsch reaction is that the use of a

4 hydrocracker can be minimized or, ideally, eliminated altogether.

5

6 While not wishing to be bound to a particular theory, the presence of ethylene

7 and other lower molecular weight olefins in the feed to the second reactor is

8 believed to compete with higher olefins. This provides a product with an

9 overall lower average molecular weight than if the reaction is done in the

10 absence of added olefins. Ethylene, in particular, is unhindered at both ends,

11 and therefore has twice the probability of starting a chain than an olefin

12 hindered at one end. Larger molecular weight olefins, while resting on the

13 catalyst bed, can either be hydrogenated to form paraffinic products that are

14 largely inert, or can compete with the smaller olefins to be incorporated into

15 the growing chain. What is generally observed is that the large olefins tend to

16 be hydrogenated rather than being incorporated into the growing chain.

17   Fischer-Tropsch Chemistry

18

19 In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by

20 contact with a Fischer-Tropsch catalyst under reactive conditions. Depending

21 on the quality of the syngas, it may be desirable to purify the syngas prior to

22 the Fischer-Tropsch reactor to remove carbon dioxide produced during the

23 syngas reaction and any sulfur compounds, if they have not already been

24 removed. This can be accomplished, for example, by contacting the syngas

25 with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a

26 packed column.

27

28 Examples of conditions for performing Fischer-Tropsch type reactions are well

29 known to those of skill in the art. Suitable conditions are described, for

30 example, in U.S. Patent Nos. 4,704,487, 4,507,517, 4,599,474, 4,704,493,

1   4,709,108, 4,734,537, 4,814,533, 4,814,534 and 4,814,538, the contents of

2   each of which are hereby incorporated by reference in their entirety.

3

4   In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on

5   a metal oxide support. The catalysts may also contain a noble metal

6   promoter(s) and/or crystalline molecular sieves. Certain catalysts are known

7   to provide chain growth probabilities that are relatively low to moderate, and

8   the product of the reaction includes a relatively high proportion of low

9   molecular (C_{2-8}) weight olefins and a relatively low proportion of high

10 molecular weight ($C_{30}+$) waxes. Certain other catalysts are known to provide

11 relatively high chain growth probabilities. Such catalysts are well known to

12 those of skill in the art and can be readily obtained and/or prepared.

13

14   Catalyst Selection

15   Catalysts with low chain growth probabilities

16

17 For the first stage of the Fischer-Tropsch reaction, any catalyst that provides

18 relatively low to moderate chain growth probabilities can be used. Typically,

19 catalysts with an alpha value between about 0.600 and 0.700 provide low

20 chain growth probabilities. Catalysts with an alpha value between about

21 0.700 and 0.800 provide moderate chain growth probabilities. Preferable

22 catalysts are those which tend to provide high yields (i.e., greater than about

23 20, and, more preferably, greater than about 30 percent by weight of the

24 products other than methane) of light (C_{2-8}) alpha olefins.

25

26 Preferably, the catalyst used in the first stage is an iron-containing catalyst.

27 Iron itself can be used and, when iron oxides are formed, can be reduced with

28 hydrogen back to iron. However, because the presence of iron fines in the

29 product stream is not preferred, and because iron oxides (rust) decrease the

30 surface area of the catalyst available for reaction, other iron-containing

31 catalysts may be preferred. Examples of suitable iron-containing catalysts

1 include those described in U.S. Patent No. 4,544,674 to Fiato et al. and Xu
2 et al., pp. 47-53, *Chemtech* (Jan. 1998).
3
4 In a preferred embodiment, the iron catalysts include at least about 10 to
5 about 60 weight percent iron. More preferably, they include between about 20
6 to about 60 weight percent iron, and most preferably about 30 to about
7 50 weight percent iron. These catalysts can be unsupported, but are
8 preferably promoted with a refractory metal oxide (SiO_2, Al_2O_3, etc.), alkali (K,
9 Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually
10 calcined, but usually are not reduced. Rather they are brought up to reaction
11 temperature directly in the CO/H_2 feed.
12
13 Co-precipitated iron-based catalysts, including those containing cobalt, can be
14 used. High levels of cobalt in an iron-cobalt alloy are known to produce
15 enhanced selectivity to olefinic products, as described, for example, in Stud.
16 Surf. Sci. Catal. 7, Pt/A, p. 432 (1981).
17
18 Examples of co-precipitated iron-cobalt catalysts and/or alloys include those
19 described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and
20 2,735,862; *AICHE* 1981 Summer Nat'l Meeting Preprint No. 408, "The
21 Synthesis of Light Hydrocarbons from CO and H_2 Mixtures over Selected
22 Metal Catalysts" ACS 173rd Symposium, Fuel Division, New Orleans, March
23 1977; *J. Catalysis* 1981, No. 72(1), pp. 37-50; Adv. Chem. Ser. 1981, 194,
24 573-88; Physics Reports (Section C of Physics Letters) 12 No. 5 (1974)
25 pp. 335-374; UK patent application No. 2050859A; *J. Catalysis* 72, 95-110
26 (1981); Gmelins Handbuch der Anorganische Chemie 8, Auflage (1959),
27 pg. 59; Hydrocarbon Processing, May 1983, pp. 88-96; and Chem. Ing. Tech.
28 49 (1977) No. 6, pp. 463-468.
29
30 Methods for producing high surface area metal oxides are described, for
31 example, in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969)
32 by P. Courte and B. Delmon. Metal oxides with a high surface area are

1   prepared by evaporating to dryness aqueous solutions of the corresponding

2   glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was

3   prepared was $CoFe_2O_4$.

4

5   Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic

6   ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction

7   and carbiding (see, for example, U.S. Patent No. 4,544,674 to Fiato et al.).

8   These catalysts tend to exhibit high activity and selectivity for C_2–C_6 olefins

9   and low methane production.

10

11   The contents of each of the patents and publications referred to above is

12   hereby incorporated by reference.

13

14   <u>Catalysts with high chain growth probabilities</u>

15

16   For the second stage of the Fischer-Tropsch chemistry, any catalyst that

17   provides relatively high chain growth probabilities can be used. Preferably,

18   the catalyst used in the second stage is a cobalt-containing catalyst.

19   Ruthenium is also an effective Fischer-Tropsch catalyst, but is more

20   expensive.

21

22   One suitable cobalt catalyst that can be used is described in U.S. Patent

23   No. 4,579,986, as satisfying the relationship:

24

25                    $(3 + 4R) > L/S > (0.3 + 0.4R),$

26

27   wherein:

28

29   L = the total quantity of cobalt present on the catalyst, expressed as

30   mg Co/ml catalyst;

31   S = the surface area of the catalyst, expressed as m^2/ml catalyst; and

1   R = the weight ratio of the quantity of cobalt deposited on the catalyst
2   by kneading to the total quantity of cobalt present on the catalyst.
3
4   Other suitable catalysts include those described in U.S. Patent
5   Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.
6   U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture
7   of CoO, Al_2O_3 and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the
8   oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal
9   oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth
10   metal, with Mo-K on carbon being preferred.
11
12   U.S. Patent No. 4,088,671 discloses minimizing methane production by using
13   a small amount of ruthenium on a cobalt catalyst. Supported ruthenium
14   catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are
15   disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.
16
17   In general, the amount of cobalt present in the catalyst is between about 1
18   and about 50 weight percent of the total catalyst composition, more preferably
19   between about 10.0 and 25 weight percent.
20
21   Preferably, the catalyst contains between about 3 and 60 ppw cobalt, between
22   0.1 and 100 ppw of at least one of zirconium, titanium or chromium per
23   100 ppw of support (typically, silica, alumina, or silica-alumina and mixtures
24   thereof).
25
26   Catalyst Supports
27
28   The type of support used can influence methane production. Suitable metal
29   oxide supports or matrices which can be used to minimize methane
30   production include alumina, titania, silica, magnesium oxide, alkaline earth
31   titanates, alkali titanates, rare earth titanates and mixtures thereof.
32

1 Methane production can be decreased using supported ruthenium catalysts.

2 Titania or titania-containing supports provide lower methane production than,

3 for example, silica, alumina or manganese oxide supports. Accordingly,

4 titania and titania-containing supports are preferred.

5

6 Typically, the catalysts have a particle size of between 10 and 110 microns,

7 preferably between 20 and 80 microns, more preferably between 25 and

8 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably

9 between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the

10 above-mentioned catalytic metals, preferably including iron in the first stage

11 and cobalt in the second stage, on one of the above-mentioned catalyst

12 supports. Preferably, the cobalt-containing catalysts include about 10 to

13 14 percent cobalt on a low density fluid support, for example, alumina, silica

14 and the like, having a density within the ranges set forth above for the

15 catalyst.

16

17 Promoters and Noble Metals

18

19 Methane selectivity is also influenced by the choice of promoter. Alkali metal

20 promoters are known for reducing the methane selectivities of iron catalysts.

21 Noble metals, such as ruthenium, supported on inorganic refractory oxide

22 supports, exhibit superior hydrocarbon synthesis characteristics with relatively

23 low methane production. Where a noble metal is used, platinum and

24 palladium are generally preferred. Accordingly, alkali metal promoters and/or

25 noble metals can be included in the catalyst bed of the first stage provided

26 that they do not significantly alter the reaction kinetics from slow chain growth

27 probabilities to fast chain growth probabilities.

28

29 Manganese Salts

30

31 The tendency for olefins to be readily hydrogenated on the cobalt catalyst

32 tends to minimize the overall yield of C_5+ products. The presence of

1 manganese and manganese salts in the catalyst and/or support tends to

2 decrease the rate of olefin hydrogenation, and, for this reason, is preferred.

3 Examples of suitable manganese-containing materials that can be used

4 include manganese-containing zeolites, unsupported and alumina-supported

5 manganese oxide catalysts, manganese molybdate. Examples of manganese

6 oxide-containing catalysts and/or supports include MnO, Al_2O_3-MnO,

7 SiO_2-MnO, MnO-carbon, Group IVB-manganese oxides, Group VB-

8 manganese oxides, Group IA (alkali metal)-manganese oxides, Group IIA

9 (alkaline earth metal)-manganese oxides and rare earth-manganese oxides

10 and mixtures thereof. The preferred support is manganese oxide.

11

12 Suitable manganese-containing catalysts are described, for example, in U.S.

13 Patent Nos. 4,206,134 and 5,162,284. When these catalysts are used in

14 Fischer-Tropsch chemistry under certain conditions, Cu-promoted Co_2MnO_4

15 showed an increased olefin content in the products versus Cu-promoted

16 Co_3O_4. U.S. Patent No. 4,206,134 discloses using MnO-supported Ru

17 catalysts which also show this effect. U.S. Patent No. 4,624,968 discloses

18 using an iron/manganese/potassium catalyst in Fischer-Tropsch synthesis.

19 These catalysts are suitable for use in the first stage Fischer-Tropsch

20 reaction.

21

22 Catalysts in spinel form have been formed which include cobalt and

23 manganese, in particular, copper-promoted cobalt-manganese spinels with

24 the formula $Co_{3-x}MnO_4$ where x is from about 0.5 to about 1.2, preferably

25 from about 0.7 to about 1.0, most preferably about 1.0. The ratio of cobalt to

26 manganese in the spinel is between about 1.5:1 and about 5:1. The amount

27 of copper promoter in the composition is preferably from about 0.1 to about

28 5 gram atom percent based on the total gram atoms of cobalt and manganese

29 of the dry composition, more preferably from about 0.5 to about 2.0 weight

30 percent. Copper-promoted cobalt-manganese catalysts appear to be

31 significantly more active, and also better at minimizing olefin hydrogenation,

1   than analogs promoted with copper but not containing manganese, or

2   catalysts containing manganese but not promoted with copper.

3

4   Ruthenium-containing catalysts can be used with manganese oxide, other

5   manganese-containing oxides or mixtures of various manganese oxides as a

6   catalyst support. These catalysts are suitable for use in the second stage

7   Fischer-Tropsch reaction.

8

9   The disclosures of each of the patents and articles discussed above are

10   incorporated herein by reference in their entirety.

11

12   <u>Synthesis Gas</u>

13

14   Typically, the synthesis gas will contain hydrogen and carbon monoxide, and

15   may include minor amounts of carbon dioxide and/or water. In the first stage,

16   the ratio of hydrogen/carbon monoxide is between about 0.5 and 1.0,

17   preferably around 0.5. In the second stage, the ratio of hydrogen/carbon

18   monoxide is preferably greater than 1.0, more preferably between about 1.0

19   and 2.0, still more preferably between about 1.0 and 1.5. A hydrogen/carbon

20   monoxide ratio of 1.0 or less results in the formation of a relatively large

21   proportion of oxygenated products, and for this reason, should be avoided.

22   Ratios above about 1.5 tend to hydrogenate a relatively large portion of the

23   olefins in the second stage before they can participate in chain growth

24   reactions. Although the amount of hydrogen tends to increase in the first

25   stage as carbon monoxide is consumed, additional hydrogen can be added to

26   achieve a desired ratio. The syngas feed in the second stage can be adjusted

27   to provide suitable ratios of hydrogen to carbon monoxide. The syngas feed

28   in the second stage is also preferably adjusted to give a ratio of olefins/CO of

29   between about 0.05 and 0.5 by weight. Below ratios of about 0.05, there

30   tends to be not enough olefin to get a significantly useful effect.

31

Operating Conditions

The first stage of the Fischer-Tropsch reaction is typically conducted at temperatures between about 270°C and 280°C, at a pressure of between about 1 and 20 ATM, in a slurry reactor or a fluidized bed reactor. Typical synthesis gas linear velocity ranges in the reactor are between about 2 and 40 cm per sec., preferably between about 6 and 10 cm per sec. After the first stage, the mixture is preferably cooled to less than 100°C, more preferably below about 80°C, and still more preferably below about 70°C. When the mixture is cooled, water and optionally a C_5+ fraction can be removed.

The resulting reaction mixture includes C_{2-4} olefins and paraffins, C_5+ products, and about 40% by weight syngas. The products in the C_{2-4} range are typically present in a ratio of about 75% olefins/25% paraffins by weight. The product mixture also tends to include water and about 5% carbon dioxide and 5% methane by weight. The reaction mixture is then added to the second stage Fischer-Tropsch reactor with additional syngas.

The second stage of the Fischer-Tropsch reaction is typically conducted in either a fixed bed reactor or a slurry reactor, where slurry reactors are preferred. The operating temperature of the fixed bed reactor is between about 200°C and 225°C, and the operating temperature of the slurry reactor is between about 225°C and 250°C, with a temperature around 240°C preferred. Typical synthesis gas linear velocity ranges in the reactor are from about 2 to 40 cm per sec., preferably from about 6 to 10 cm per sec. The pressure is preferably between about 1 and 30 ATM, with pressures between 20 and 30 ATM being particularly preferred. Above about 30 ATM, carbonyls may be formed and, therefore, pressures significantly about 30 ATM are not preferred. Further, the rate of reaction tends to increase with increased pressure, but tends to level off due to hydrodynamic problems at around 30 ATM.

1 The catalyst space velocities are typically between about 100 and

2 10,000 cc/g/h, preferably between about 300 and 3,000 cc/g/h, for both

3 stages.

4

5 Following the second stage, the reaction mixture is preferably cooled to less

6 than 100°C, and liquid products are trapped. Methane is preferably bled off to

7 a syngas generator and recycled. Water is preferably removed.

8

9 As discussed above, slurry reactors can be preferred for one or both of the

10 stages. Bubble column slurry reactors can be particularly preferred. Details

11 regarding bubble column slurry reactors can be found, for example, in Y. T.

12 Shah et al., Design Parameters Estimations for Bubble Column Reactors,

13 *AIChE Journal*, 28 No. 3 pp. 353-379 (May 1982); Ramachandran et al.,

14 Bubble Column Slurry Reactor, Three-Phase Catalytic Reactors Chapter 10,

15 pp. 308-332 Gordon and Broch Science Publishers (1983); Deckwer et al.,

16 Modeling the Fischer-Tropsch Synthesis in the Slurry Phase, Ind. Eng. Chem.

17 Process Des. Dev. v 21, No. 2, pp. 231-241 (1982); Kölbel et al., The

18 Fischer-Tropsch Synthesis in the Liquid Phase, Catal. Rev.-Sci. Eng., v.

19 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982, the contents of

20 each of which are hereby incorporated by reference in their entirety.

21

22 Since the catalyst metal may be present in the catalyst in the form of an oxide,

23 the catalyst may be reduced with hydrogen prior to contact with the slurry

24 liquid. The starting slurry liquid is typically a heavy hydrocarbon that is

25 viscous enough to keep the catalyst particles suspended (typically a viscosity

26 between 4 and 100 centistokes at 100°C) and a low enough volatility to avoid

27 vaporization during operation (typically an initial boiling point range of

28 between about 350°C and 550°C). The slurry liquid is preferably essentially

29 free of contaminants such as sulfur, phosphorous or chlorine compounds.

30 Initially, it may be desirable to use a synthetic hydrocarbon fluid such as a

31 synthetic olefin oligomer as the slurry fluid.

1 Often, a paraffin fraction of the product having the desired viscosity and

2 volatility is recycled as the slurry liquid. The slurry typically has a catalyst

3 concentration of between about 2 and 40 percent catalyst, preferably between

4 about 5 and 20 percent, and more preferably between about 7 and 15 percent

5 catalyst based on the total weight of the catalyst, i.e., metal plus support.

6

7 Preferably, each reactor converts about 60% or more of the syngas to

8 products, and the overall yield is preferably about 80% or greater, more

9 preferably, about 90% or greater. In the first stage, above about 60%

10 conversion, carbon dioxide production tends to increase, which is not

11 preferred. The conversion in the second stage can go higher than about 60%.

12 The product distribution tends to be about 50% hydrocarbons boiling in the

13 diesel range, with up to 70% between C_5 and C_{20}, and with about 15% or less

14 in the C_{1-4} range, and about 15% or less in the C_{20-50} range.

15

16 Although the stages described herein are described in terms of a

17 Fischer-Tropsch reaction, these stages can optionally be performed using

18 various modifications of the literal Fischer-Tropsch process where hydrogen

19 (or water) and carbon monoxide (or carbon dioxide) are converted to

20 hydrocarbons (e.g., paraffins, ethers, etc.). Thus, the term Fischer-Tropsch

21 type product or process is intended to apply to Fischer-Tropsch processes

22 and products and the various modifications thereof and the products thereof.

23 For example, the term is intended to apply to the Kolbel-Engelhardt process

24 typically described by the reaction:

25

26 $$3CO + H_2O \rightarrow -CH_2- + 2CO_2$$

27
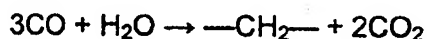
28 The CO_2 product can be returned to the syngas generator and combined with

29 methane (and some air) to form additional syngas.

30

1 The Separation of Product From the Fischer-Tropsch Reaction

2

3 The products from Fischer-Tropsch reactions generally include a gaseous

4 reaction product and a liquid reaction product. The gaseous reaction product

5 includes hydrocarbons boiling below about 650°F (e.g., tail gases through

6 middle distillates). The liquid reaction product (the condensate fraction)

7 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil

8 through heavy paraffins).

9

10 The minus 650°F product can be separated into a tail gas fraction and a

11 condensate fraction, i.e., about C_5 to C_{20} normal paraffins and higher boiling

12 hydrocarbons, using, for example, a high pressure and/or lower temperature

13 vapor-liquid separator or low pressure separators or a combination of

14 separators.

15

16 The fraction boiling above about 650°F (the condensate fraction) is typically

17 separated into a wax fraction boiling in the range of about 650°F-1200°F after

18 removing particulate catalyst fines and one or more fractions boiling above

19 about 1200°F. The wax fraction primarily contains C_{20} to C_{50} linear paraffins

20 with relatively small amounts of higher boiling branched paraffins. Typically,

21 the separation is effected by fractional distillation.

22

23 Optional Process Steps

24

25 The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic

26 contaminants in the feedstock is undesirable. For this reason, it is preferred

27 to remove sulfur and other contaminants from the feed before performing the

28 Fischer-Tropsch chemistry. Means for removing these contaminants are well

29 known to those of skill in the art. For example, ZnO guardbeds are preferred

30 for removing sulfur impurities. Means for removing other contaminants are

31 well known to those of skill in the art.

1   In one embodiment, any methane produced by the reaction is recovered and

2   converted to synthesis gas for recycling in the process. Alternatively, the

3   entire product stream from the first reactor can be added to the second

4   reactor.

5

6   In some embodiments, the product stream from the second stage may contain

7   a relatively large amount of olefins that can be hydrogenated following the

8   Fischer-Tropsch chemistry. Optionally, these olefins can be isomerized prior

9   to hydrogenation to provide branched paraffins. Branching may be

10   advantageous in a number of end-uses, particularly when increased octane

11   values (when the compositions are used as fuels) or decreased pour points

12   are desired.

13

14   After the reaction mixture is converted to the final product stream, the desired

15   products can be isolated, for example, by distillation. C_{1-4} products can be

16   obtained and used to form synthesis gas for subsequent use in the process

17   described herein. C_{5-12} products can be isolated and used, for example, as

18   combustible fuels.

19

20   Higher molecular weight products can either be isolated and used directly, or

21   can be reacted to form lower molecular weight products, as desired. For

22   example, high molecular weight products can be hydrocracked to provide

23   lower molecular weight products, increasing the yield of liquid combustible

24   fuels.

25

26   Hydrocracking refers to a catalytic process, usually carried out in the

27   presence of free hydrogen, in which the cracking of the larger hydrocarbon

28   molecules is a primary purpose of the operation. Desulfurization and/or

29   denitrification of the feed stock usually will also occur.

30

31   Catalysts used in carrying out hydrocracking operations are well known in the

32   art, and it should not be necessary to describe them in detail here. See, for

1   example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions

2   of hydrotreating, hydrocracking, and typical catalysts used in each process.

3   The product from the hydrocracking can be subject to distillation and/or

4   catalytic isomerization to provide lube oils, diesel fuel, and the like.

5

6   Optionally, an acid catalyst can be added to the reaction mixture in either

7   stage, but preferably in the second stage. When C_4+ alpha-olefins are

8   produced, the alpha-olefins isomerize to more substituted olefins in the

9   presence of the acid catalyst. This reduces the chain growth probability for

10   C_4+ and largely minimizes wax formation.

11

12   The process will be readily understood by referring to the flow diagram in

13   Figure 4. In Figure 4, a mixture of carbon monoxide and hydrogen (syngas) is

14   added to a first stage Fischer-Tropsch reactor (Box 10). The products are

15   cooled, water is removed and the C_5+ fraction is isolated via distillation (Box

16   40) and contained in Box 20. The C_{1-4} fraction and additional syngas is sent

17   to a second stage Fischer-Tropsch reactor (Box 30). The product of the

18   reaction is fractionally distilled (Box 40). The C_{1-4} fraction is sent to a syngas

19   generator (Box 50). The C_{5-20} fraction is collected (Box 20) separately from

20   the C_{20}+ fraction, which is optionally hydrocracked and/or hydrotreated

21   (Box 60). In the flow scheme contained in Figure 4, the process of the

22   present invention is practiced in continuous operation. However, it is possible

23   to practice the present invention in batch operation.

24   The following example will help to further illustrate the invention but are not

25   intended to be a limitation on of the scope of the process.

26

1	**Example 1**
2	Addition of ethylene to a Cobalt-Catalyzed Fischer-Tropsch Reaction
3	
4	**EXPERIMENTAL**
5	CRLA -2B Catalyst
6	The catalyst had a nominal composition of 20 wt. % Co, 0.5 wt. % Ru, 1 wt. %
7	La_2O_3, and 78.5 wt. % Al_2O_3. It was prepared from a Ketjen fluid alumina by
8	suspending the alumina in a hot (80°C) aqueous solution of the nitrate salts of
9	Co, Ru, and La (nitrosyl nitrate for Ru). A hot aqueous solution of potassium
10	carbonate was added to the suspended alumina with vigorous stirring. The
11	metals then precipitated onto the support as hydroxides. The solids were
12	filtered and washed several times with hot distilled water, then calcined in a
13	fluid bed reactor by heating them slowly in air to 300°C. They were cooled to
14	room temperature, then reduced by heating them slowly (1°C/min.) to 350°C
15	in pure hydrogen at atmospheric pressure. The reducing gas flow equaled or
16	exceeded 1800 cc/g/h. After cooling and purging with nitrogen, the reduced
17	catalyst was passivated by adding enough dilute air at ambient temperature to
18	reoxidize the metals completely, at a slow enough rate that the oxidation
19	exotherm did not exceed 50°C. A hydrogen TPD test indicated that the Co
20	dispersion of the catalyst was about 10%.
21	
22	Tests with Pure Synthesis Gas
23	Tests of the fluid catalyst were made on 4-gram quantities of the fluid particles
24	in a fixed bed reactor after they were diluted with an equal volume of 0.5 mm
25	glass beads. The temperature control was within ±1°C under all conditions.
26	Activation was done in hydrogen at atmospheric pressure at a flow rate of
27	1800 cc/g/h. The heating rate was 1°C/min. to 350°C and the hold at that
28	temperature was two hours. After activation, the catalyst was cooled in
29	hydrogen to 185°C for the start of the synthesis run. Initial startup was at
30	185°C and 1 atm with a 900 cc/g/h flow of synthesis gas having $H_2/CO = 1.5$.

1 Those conditions were maintained for one hour before switching to the

2 experimental conditions.

3

4 ### Tests with Synthesis Gas plus Ethylene and/or Water

5 Tests with added ethylene were made after the catalyst was started up in pure

6 synthesis gas at 185°C and operated for at least one hour at that condition

7 before it was heated to 200°C. During the tests, ethylene was added at either

8 a 1:2 or 1:1 mole ratio with CO. Total flow rates were adjusted to 900 cc/g/h

9 or 1800 cc/g/h. To examine the effects of added water on Fischer-Tropsch

10 synthesis and olefin hydrogenation, inlet gases were passed through a

11 saturator held at 22°C. This produced a reactant stream containing 2.6 vol. %

12 water.

13

14 ### RESULTS

15 All experiments were run at 200°C and one atmosphere pressure.

16 Compositions of the inlet streams and flow rates for each experiment are

17 shown in Table 1 and Table 2.

Table 1. Synthesis Gas Conversion over CoRu-La$_2$O$_3$/Alumina

Temperature, °C	200	200	200	200	200	200	200	200
Pressure, atm	1	1	5	5	1	1	5	5
H$_2$/CO Ratio	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0
CO GHSV, cc/g/h	720	360	720	360	720	360	720	360
H$_2$ GHSV, cc/g/h	1080	540	1080	540	1080	540	1080	540
CO Conversion, %	33.0	53.9	52.8	72.6	20.3	29.3	29.4	44.9
CO Rate, cc/g/h	238	194	380	261	183	132	265	202
H$_2$ Conversion, %	46.2	66.7	71.6	91.0	38.9	61.7	66.8	84.7
H$_2$ Rate, cc/g/h	499	360	773	491	350	278	601	381
Product Wt%								
H$_2$O	46.9	42.7	49.7	38.0	48.4	52.5	52.0	48.1
CO$_2$	16.4	20.0	9.2	23.6	7.7	9.0	5.8	11.7
CH$_4$	9.3	8.0	8.4	8.3	6.4	6.0	5.3	4.5
C$_2$-C$_4$	10.6	10.2	7.2	6.3	8.7	8.3	6.2	5.0
C$_{5+}$	16.8	19.2	25.6	23.9	28.8	24.1	30.7	30.7
H$_2$O Rate, g/g/h	0.160	0.117	0.270	0.141	0.126	0.099	0.200	0.138
CO$_2$ Rate, g/g/h	0.056	0.055	0.050	0.087	0.020	0.017	0.022	0.034
CH$_4$ Rate, g/g/h	0.031	0.021	0.046	0.031	0.015	0.010	0.022	0.013
C$_2$-C$_4$ Rate, g/g/h	0.035	0.027	0.039	0.024	0.020	0.014	0.026	0.014
C$_{5+}$ Rate, g/g/h	0.056	0.050	0.141	0.088	0.069	0.042	0.125	0.090
Total HC Rate, g/g/h	0.122	0.098	0.226	0.143	0.104	0.066	0.173	0.117

1

Table 2. Synthesis Gas Conversion over CoRu-La$_2$O$_3$/Alumina

Temperature, °C	200	200	200	200	200	200	200	200
Pressure, atm	1	1	5	5	1	1	5	5
H$_2$/CO Ratio	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0
CO GHSV, *cc/g/h*	701	584	701	584	877	701	877	701
H$_2$ GHSV, *cc/g/h*	1052	877	1052	877	877	701	877	701
C$_2$H$_4$ GHSV, *cc/g/h*	0	292	0	292	0	351	0	351
H$_2$O GHSV, *cc/g/h*	47	47	47	47	47	47	47	47
CO Conversion,	30	19	32	33	17	14	22	22
C$_2$H$_4$ Conversion, %	...	67	...	75	...	51	...	67
C$_2$H$_4$ to C$_3$+, %	...	44	...	35	...	48	...	50
H$_2$ Conversion, %	45	39	46	62	35	40	67	69
Product Weight,								
H$_2$O	50	28.9	46.9	40.1	41.4	29.8	45.9	33.4
CO$_2$	11.2	5.3	5.6	6.3	23.9	11.6	4.7	4.4
CH$_4$	9.5	6	7.7	4.9	7.6	4.3	5.5	3.2
C$_2$-C$_4$	11.2	23.2	8	10.4	10.3	22.1	6.4	11.1
C$_{5+}$	18.2	36.5	31.8	38.3	16.9	32.3	37.5	48
Product Rates								
H$_2$O Rate, *g/g/h*	0.132	0.058	0.152	0.147	0.100	0.075	0.117	0.115
CO$_2$ Rate, *g/g/h*	0.026	0.024	0.018	0.023	0.041	0.039	0.012	0.015
CH$_4$ Rate, *g/g/h*	0.016	0.012	0.025	0.018	0.019	0.011	0.014	0.011
		-0.004		-0.007		-0.008		-0.003

1

C₂-C₄ Rate, g/g/h	0.022	0.045	0.026	0.023	0.058	0.016	0.038

C₅+ Rate, g/g/h	0.048	0.063	*+0.015*	0.101	0.041	*+0.042*	0.087	*+0.046*	0.097	0.168	*+0.071*
Total CH$_x$ Rate, g/g/h	0.086	*+0.034*	0.120	0.143	*+0.047*	0.199	0.156	*+0.073*	0.127	0.217	*+0.080*

1

2   *For experiments with added ethylene, the C₂ fraction was excluded from the product analyses.*

1   **Synthesis Gas Only**

2   Results at several flow rates over the fluid CoRu catalyst operating at one

3   atmosphere and 200°C are shown in Table 1. Conversions were high for

4   these runs, and the main change with flow rate was a change in the

5   conversion level and in the amount of CO_2 that was produced. The CO

6   conversion rate increased with increasing space velocity (see Figure 1) and

7   the CO_2 formation rate increased almost linearly with increasing CO

8   conversion.

9

10   **Synthesis Gas Plus Ethylene**

11   Experiments with added ethylene were made at either 1 atm or 5 atm

12   pressure, with or without saturation of the gas feed with water. The water had

13   little effect other than to depress the CO conversion rate slightly. Data for

14   runs with added water are shown in Table 2. The H_2/CO ratio in the gas feed

15   was either 1.0 or 1.5, while the amount of added ethylene was either zero or

16   one-half the amount of CO (so that the number of moles of carbon in C_2H_4

17   and CO were equal).

18

19   In each case where ethylene was added, the hydrocarbon synthesis rate

20   increased significantly and a large portion of the C_3+ products were derived

21   from ethylene. This was not accompanied by a corresponding increase in the

22   methane formation rate. On the contrary, the formation rate for methane

23   decreased when ethylene was added (see Table 2). This would be expected

24   if the main function of ethylene is to initiate new hydrocarbon chains. In that

25   case, the fraction of C_1 species at active sites would be expected to decrease

26   as the fraction of C_2 species increases.

27

28   At one atmosphere pressure, the CO conversion rate declined when ethylene

29   was added, but at five atmospheres pressure it was relatively unaffected by

30   ethylene addition. Also, the increase in hydrocarbon synthesis rate was

31   concentrated mainly in the C_5+ fraction at 5 atm pressure, while at 1 atm

1 pressure much of the increase was in C_3 and C_4 products. These effects are

2 shown in Figure 2 and Figure 3.

3

4 The increase in C_5+ synthesis rates with ethylene addition was much more

5 pronounced at $H_2/CO = 1$ than at $H_2/CO = 1.5$ (see Table 2, Figure 2 and

6 Figure 3). Also, the fraction of ethylene incorporated into C_3+ products was

7 greater at that ratio. Thus, the best results for ethylene incorporation into

8 liquid hydrocarbons in these tests were obtained at 5 atm pressure and

9 $H_2/C_2H_4/CO = 1:0.5:1$.

10

11 Lower H_2/CO ratios would appear to favor better utilization of added ethylene

12 (less hydrogenation to ethane), but may also cause excessive CO_2 production

13 at higher conversion levels or else limit the conversion, since the usage ratio

14 is two H_2 molecules per CO molecule. The H_2/CO ratio in the reactor will drop

15 with increasing conversion, lowering the conversion rate, unless it is

16 replenished by the water gas shift reaction: $H_2O + CO \rightarrow CO_2 + H_2$. It is

17 believed that a ratio of H_2/CO of 1.0 is the lowest ratio that should be used.

1   WHAT IS CLAIMED IS:

2

3   1.   An integrated process for preparing liquid fuels, the process comprising:

4

5   (a)   subjecting syngas with a hydrogen/carbon monoxide ratio of

6   between about 0.5 and 1.0 to Fischer-Tropsch reaction conditions

7   where the catalyst used for the Fischer-Tropsch reaction is one

8   which provides low to moderate chain growth probabilities;

9

10   (b)   optionally removing water and/or C_5+ hydrocarbons from the

11   product stream;

12

13   (c)   subjecting the product from step (a) or (b) to Fischer-Tropsch

14   reaction conditions where the catalyst used for the Fischer-Tropsch

15   reaction is one which provides high chain growth probabilities,

16   where the hydrogen/carbon monoxide ratio is between about 1.0

17   and 2.0; and

18

19   (d)   isolating the product of the reaction.

20

21 2.   The process of claim 1, wherein the catalyst with low to moderate chain

22   growth probabilities is an iron-containing catalyst.

23

24 3.   The process of claim 1, wherein the catalyst with high chain growth

25   probabilities is a cobalt-containing catalyst.

26

27 4.   The process of claim 1, wherein step a) is conducted at a temperature

28   between about 270°C and 280°C and at a pressure of between about 1

29   and 20 ATM.

30

5. The process of claim 1, wherein step (a) is conducted in a slurry reactor or a fluidized bed reactor.

6. The process of claim 1, wherein the product stream is cooled to less than 100°C and at least a portion of the water produced during the reaction is removed.

7. The process of claim 1, wherein a C_5+ fraction is isolated after step (a) and before step (c).

8. The process of claim 1, wherein at least a portion of the olefins prepared in step (a) are isomerized before being subjected to the Fischer-Tropsch reaction conditions in step (c).

9. The process of claim 1, wherein step (c) is conducted at a temperature between about 200°C and 250°C and at a pressure between about 1 and 30 ATM.

10. The process of claim 1, wherein the product of step (a) in the C_{2-4} range includes about 75% olefins by weight.

11. The process of claim 1, wherein the Fischer-Tropsch reactions in steps (a) and/or (c) are run in a slurry reactor.

12. The process of claim 1, wherein olefin hydrogenation in steps (a) and/or (c) is minimized by adding a manganese-containing compound to the reaction.

13. The process of claim 1, wherein the hydrogen/carbon monoxide ratio in step (c) is between about 1.0 and 1.5.

14. The process of claim 1, wherein unreacted syngas is recycled.

15.   The process of claim 14, wherein a at least a
portion of the carbon dioxide is removed from the
syngas before it is recycled.

16.   An integrated process for preparing liquid
5   fuels, substantially as described and shown in Figure 4
of the accompanying drawings.

17.   A hydrocarbon product produced by the process
of any preceding claim.

10

Application No:	GB 0104292.8	Examiner:	Dr William Thomson
Claims searched:	1-17	Date of search:	17 May 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C5G (GAD)

Int Cl (Ed.7): C10G 2/00

Other: ONLINE: CAS-ONLINE, EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 4624968 (KIM ET AL) See whole document, in particular column 3, lines 17-49, the Example and claims 1-4	1, 2, 4, 5, 9, 12 and 13
X	Chemical Abstract No 131:353528 & CN 1137058 (B.ZHONG ET AL), 01/12/96 See abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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